Pyrolysis-Gas Chromatography/Mass Spectrometry Analysis of Paints, Tapes, and Polymers

1 Scope

This procedure applies to Chemistry Unit caseworking personnel who analyze paints and polymers via pyrolysis-gas chromatography with mass spectrometry (Py-GC/MS). This document describes the sample preparation and suggested instrumental parameters for the Py-GC/MS analysis of paints, tapes, and other polymeric materials.

2 Equipment/Materials/Reagents

a. Instrumentation - Gas Chromatograph, Mass Selective Detector with EI Source, and Software (Agilent or equivalent)

b. Autosampler - Pyrolysis Autosampler, accessories, and software (Frontier, or equivalent)

c. Sample holder: alloyed metal cups (Frontier or equivalent)

d. Cleaning and preparation apparatus for sample holders (e.g., small butane torch, sample cup inspector, sample cup holder)

e. Polymeric reference materials (Scientific Polymer Products, Inc. or equivalent)

f. Stereo-microscope (~ 6 to ~ 50x) with appropriate lighting

g. Scalpel handle with blades

h. Wire probe

i. Tweezers

j. Glass microscope slides

k. Analytical microbalance (optional)

l. Cleaning solvent (e.g., methanol, chloroform) - Reagent grade or equivalent

3 Standards and Controls

3.1 Standards

Manufacturer-supplied and commercially available paints, tapes, polymers, adhesives, and sealants are maintained in within the FBI Laboratory. These materials are used in casework in accordance with the *Chemistry Unit Procedures for the Use of Reference Materials and Known Materials*.

3.2 Performance Checks

Refer to the *Performance Monitoring Protocol (QA/QC) for the Pyrolysis-GC/MS (Py-GC/MS)* for details on the performance checks and necessary supplies to conduct these checks and operate the instrument.

4 Sampling

Refer to the current version of the relevant material's *General Approach* Paints and Polymers Standard Operating Procedure (P&P SOP) (e.g., PPSU100, PPSU 101, PPSU 102) for guidance as to how samples are selected for analysis and comparison. Record the sample(s) selected for analysis in the case notes.

5 Procedure

1) Using a scalpel or similar tool, prepare a clean[1] sample of material large enough (approximately 50 µg) to provide an adequate signal. The amount can vary depending on instrument sensitivity and chemical composition of the material (e.g., amount of inorganic filler, type of binder).

    a. Separate individual components (e.g., paint layers, backings, adhesives) by taking thin peels with a scalpel.

    b. Multi-layer samples can be analyzed if it is not possible to separate layers.

    c. If appropriate, sample dried material (e.g., cured spray paint on the nozzle) from the container of an uncured specimen. Alternatively, a portion of an uncured sample (e.g., glues, two-part adhesive systems, liquid paint) can be mixed, applied to a clean microscope slide or other suitable substrate, and permitted to dry/harden according to the manufacturer's recommendations.

[1] "Clean" is defined as either 1) an inner core sample; 2) a sample cleaned with an appropriate solvent; or 3) a sample void of contamination from components that exist within the same environment.

2) Place the sample in an appropriate container for analysis. Proper and consistent placement of the sample within the base of the sample cup is critical for complete pyrolysis and reproducibility of data.

3) Verify that the daily and monthly performance monitoring procedures have been conducted and appropriately recorded in the relevant case notes. See the instrument SOP entitled *Performance Monitoring (QA/QC) Protocol for the Pyrolysis-GC/MS (Py-GC/MS)* for specific details.

4) Analyze the performance standard, sample(s), and blanks by Py-GC/MS using the suggested instrumental parameters below. At a minimum, one blank is placed before and after each standard, sample, or reference material analyzed.

5) If identification of the pyrolyzates is warranted, known standards can be analyzed under the same instrumental conditions used for sample analysis.

6) Evaluate the data using the decision criteria below.

6 Instrumental Conditions

The following instrumental conditions are a guide for all standards and samples described in this SOP, and as such, are set within the instrument method but are not necessarily exact values. The method used is retained with the case record (e.g., printed and stored in the case notes).

Pyrolysis GC/MS(EI):

Pyrolysis Autosampler:	
Interface Set Point:	300˚C
Furnace Temp:	600˚C
Furnace Hold Time:	0.20 min

GC Oven:	
Initial Temp:	50˚C
Initial Time:	2 minutes
Ramp Rate:	13˚C/minute
Final Temp:	325 ˚C
Final Hold Time:	15 minutes
Run Time:	38.154 minutes

GC Inlet:	
Mode:	Split
Split Ratio:	50:1
Inlet Temp:	300˚C
Split Flow:	35 mL/min
Carrier:	Helium
Init Flow:	0.7 mL/min
Flow Mode:	Constant flow
Septum purge:	3mL/min

GC Column:	
Type:	HP-5 or equivalent
Length:	40 m
Diameter:	250 µm
Film Thickness:	0.25 µm

MS Parameters:

Source Temp: 230˚C		Ionization Mode:	Electron Impact
Transfer Line Temp: 300 ˚C			
Scan Mode: Full Scan		Scan Range:	34-650 m/z

7 Decision Criteria

The following criteria are used as a guide in determining the acceptability of the data produced in this procedure. Retention time, peak shape, relative intensity, and the presence/absence of corresponding diagnostic peaks are all evaluated. Examples of diagnostic peaks would be those that aid in the classification or identification of the polymer based on the components present.

7.1 Blanks

a. The blank run before each sample is evaluated for the presence of carry-over peaks from the previous sample. It is also evaluated for system peaks that could contribute to a sample's signal, possibly hindering appropriate evaluation of true peaks that are present. Ideally, the blank preceding the sample should not exhibit any chromatographic peaks greater than the CO_2 response. If extraneous peaks are noted, document that the peak was considered as well as the results of the evaluation.

7.2 Samples

a. For characterization of an unknown sample, compare the data (pyrogram and mass spectrum) for the unknown sample with respect to a known reference material or mass spectral library.

b. For comparisons of evidentiary samples, compare pyrograms side-by-side or using overlays. Compare the retention times and corresponding mass spectral data.

c. As applicable, assess heterogeneity, sample size, or reproducibility of the pyrolysis process through the analysis of replicates.

d. The presence of additional peaks could be inherent differences between samples, from contamination or carry-over, or system peaks (e.g., siloxanes). Document that the peak was considered and the possible explanations for why those peaks were present. If the additional peaks are explainable as contamination, carry-over, or system peaks, then they are not exclusionary differences.

e. Sample comparisons should be conducted with pyrograms collected using similar sample preparations, similar sample characteristics (e.g., quantities, single layers vs multilayered samples), and similar instrumental parameters, as appropriate.

f. Pyrograms are compared and interpreted based on the observation of any chromatographic differences, or lack thereof, between the sets of data.

    i. Chromatographic overlay is a recognized approach for comparing data where the presence or absence of peaks, peak shapes, and relative intensities are all considered in the evaluation as to whether exclusionary differences exist between compared samples.

    ii. When assessing differences between pyrograms, consider sample limitations (e.g., small samples, dirty samples) and instrumentation limitations (e.g., sampling size, limits of detection).

g. Possible reasons for chromatographic or mass spectral differences include dissimilar sample conditions (e.g., quantities, contamination from adjacent layers), lack of representativeness of the specimen or source material, contribution from extraneous materials, or origination from different source materials. Additional samples can provide supplemental data to assist in assessing such differences.

h. If suitable pyrograms are produced, comparisons can provide information regarding the potential relationship of the sources of the samples.

    i. Distinguishable sources: When exclusionary differences are observed between compared chromatographic features, the sources of the samples are considered distinguishable by pyrolysis GC/MS. Exclusionary differences in chromatographic or mass spectral comparisons: 1) are outside the variability of data originating from the same source; and 2) cannot be explained by considerations such as sample heterogeneity, contamination, different sample conditions, or different sample histories.

    ii. Indistinguishable sources: When no exclusionary differences are observed between compared chromatographic or mass spectral features, the sources of the samples are considered indistinguishable by pyrolysis GC/MS. Differences that are not considered exclusionary: 1) are within the variability of data originating from the same source; or 2) can be explained by considerations such as sample heterogeneity, contamination, different sample conditions, or different sample histories. If no exclusionary differences are observed in a py-GC/MS comparison, samples can be analyzed by other analytical techniques to provide additional information about the potential relationship between the sources of the samples.

i. Py-GC/MS is one part of a multi-analytical comparative approach. This data alone can be used to distinguish the sources of compared samples, but otherwise is not used independent of data obtained from other analytical techniques to reach an overall opinion regarding the potential relationship between the sources of the samples. An overall

opinion that sources are indistinguishable is only reported when no exclusionary differences are observed in the analytical techniques that were applied.

8 Calculations

Not applicable.

9 Measurement Uncertainty

Not applicable.

10 Limitations

a. Pyrolysis-gas chromatography/mass spectrometry is a destructive analytical technique.

b. Sample size or condition may preclude examination by this technique.

c. The information obtained from the analysis of combined layers of a multi-layer paint chip will hinder the ability to discriminate between the individual layers.

11 Precautionary Statements

a. As with any procedure involving trace evidence, ensure actions minimize the potential for loss or contamination of the sample.

b. When conducting comparative analysis of two or more samples, care must be taken to ensure that each specimen to be compared is present in approximately the same amount. Unequal sampling can result in relative intensity differences within this analytical technique.

c. In a multi-layer material, care must be taken to ensure that each specimen is free of contribution from unwanted adjacent layers.

d. Care must be taken during sample preparation to ensure consistency of sample placement within the bottom of the sample vessel.

12 Safety

Use standard precautions for the handling of potentially biohazardous materials, chemicals, or sharps. Refer to the FBI Laboratory Safety Manual and appropriate Safety Data Sheet(s) for further details.

References

1) Bakowski, N.L., Bender, E.C., Munson, R.O. Comparison and identification of adhesives used in improvised explosive devices by pyrolysis-capillary column gas chromatography-mass spectrometry. *J. Anal. Applied Pyrolysis* 1985; 8: 483-492.

2) Blackledge, R.D. Application of pyrolysis gas chromatography in forensic science. *For. Sci. Rev.* 1992; 4(1): 1-16.

3) Challinor, J.M. Forensic applications of pyrolysis capillary gas chromatography. *For. Sci. Int.* 1983; 21: 269-285.

4) Challinor, J.M. Pyrolysis techniques for the characterization and discrimination of paint. In: *Forensic Examination of Glass and Paint; Analysis and Interpretation*, B. Caddy, ed., Taylor & Francis, London, England, 2001.

5) Curry, C.J. Pyrolysis-mass spectrometry studies of adhesives. *J. Anal. Applied Pyrolysis* 1987; 11: 213-225.

6) Procedures for the Use of Reference Materials and Known Materials, FBI Laboratory, Chemistry Unit Quality Assurance Manual.

7) FBI Laboratory Safety Manual.

8) Kochanowski, B.K., Morgan, S.L. Forensic discrimination of automotive paint samples using pyrolysis-gas chromatography-mass spectrometry with multivariate statistics. *J. Chrom. Sci.* 2000; 38: 100-108.

9) Learner, T.J.S. *Analysis of Modern Paints*. The Getty Conservation Institute, Research in Conservation series, Los Angeles: 2004.

10) Levy, E.J. The analysis of automotive paints by pyrolysis-gas chromatography. *J. For. Sci. Soc.* 1976; 5: 102-109.

11) McMinn, D.G.; Carlson, T.L.; Munson, T.O. Pyrolysis capillary gas chromatography/ mass spectrometry for analysis of automotive paints. *J. For. Sci.* 1985; 30(4): 1064-1073.

12) Mehltretter, A.H., Bradley, M.J., Wright, D.M. Analysis and discrimination of electrical tapes: Part I. Adhesives, *J Forensic Sci.*, 2011, 56(1):82-94

13) Mehltretter, A.H., Bradley, M.J., Wright, D.M. Analysis and discrimination of electrical tapes: Part II. Backings, *J Forensic Sci.*, 2011; 56(6): 1493-1504

14) Nielsen, H.K.R. Forensic analysis of coatings. *J. Coat. Tech.* 1984; 56(718): 21-32.

15) Noble, W; Wheals, B.B.; Whitehouse, M.J. The characterization of adhesives by pyrolysis gas chromatography and infrared spectroscopy. *Forensic Science* 1974; 3: 163-174.

16) Phair, M., Wampler, T.P. Analysis of rubber material by pyrolysis GC. *Rubber World* Feb. 1997: 30-34.

17) Plage, B., Berg, A., and Luhn, S. The discrimination of automotive clear coats by pyrolysis-gas chromatography/mass spectrometry and comparison of samples by a chromatogram library software. *For. Sci. Int.* 2008; 177: 146-152.

18) *Performance Monitoring Protocol (QA/QC) for the Pyrolysis-GC/MS (Py-GC/MS)*, FBI Laboratory, Chemistry Unit - Instrument Operation and Systems Support SOP

19) Russell, J., Singer, B.W., Perry, J.J. The identification of synthetic organic pigments in modern paints and modern paintings using pyrolysis-gas chromatography-mass spectrometry. *Anal Bioanal Chem* 2011; 400: 1473-1491.

20) Ryland, S.G. Infrared microspectroscopy of forensic paint evidence. Chapter 6 in *Practical Guide to Infrared Microspectroscopy*. (ed. H.J. Humecki) NY: Marcel Dekker, Inc., 1995.

21) Ryland, S.G., Jergovich, T.A. and Kirkbride, K.P. Current trends in forensic paint examination. *Forensic Sci Rev*, 2006; 18(2):97-117.

22) Ryland, S.G., Suzuki, E.M., Analysis of paint evidence. In: *Forensic Chemistry Handbook* (ed. L. Kobilinsky), NY: Wiley and Sons, 2012.

23) Saferstein, R. Forensic aspects of analytical pyrolysis. In: *Pyrolysis and GC in Polymer Analysis* (eds. S.A. Leibman and E.J. Levy) NY: Marcel Dekker, Inc., 1985.

24) Sakayanagi, M., Konda, Y., Watanabe, K., and Harigaya, Y. Identification of pressure-sensitive adhesive polypropylene tape. *J Forensic Sci* 2003; 48(1):68-76.

25) Scientific Working Group for Materials Analysis (SWGMAT). Standard Guide for Using Pyrolysis Gas Chromatography and Pyrolysis Gas Chromatography/Mass Spectrometry in Forensic Paint Examinations. *JASTEE* 2014; 5(1):22-33.

26) Scientific Working Group for Materials Analysis (SWGMAT). Standard Guide for Using Pyrolysis Gas Chromatography and Pyrolysis Gas Chromatography/Mass Spectrometry in Forensic Tape Examinations. *JASTEE* 2014; 5(1):42-50.

27) Tsuge, S., Ohtani, H., Watanabe, C. *Pyrolysis-GC/MS Data Book of Synthetic Polymers* Oxford: Elsevier, 2011.

28) Wampler, T.P. *Applied Pyrolysis Handbook.* 2nd ed. Boca Raton, FL: CRC Press, 2007.

29) Wampler, T.P., Bishea, G.A., Simonsick, W.J. Recent changes in automotive paint formulation using pyrolysis-gas chromatography/mass spectrometry for identification. *J. Anal. Applied Pyrolysis* 1997; 40-41: 79-89.

30) Wampler T.P., Zawodny C.P. Analysis of polymer packing products using pyrolysis-gas chromatography-mass spectrometry. *Am. Lab. News Ed.* 1999; 31(19): 30-32.

31) Wampler, T.P. Introduction to pyrolysis-capillary gas chromatography. *J. Chrom. A* 1999; 842: 207-220.

32) Williams, E.R., Munson, T.O. The comparison of black polyvinylchloride (PVC) tapes by pyrolysis gas chromatography. *J. For. Sci.* 1988; 33(5): 1163-1170.

33) Wright, D.M., Bradley, M.J., Mehltretter, A.H. Analysis and discrimination of architectural paint samples via a population study, *Forensic Sci. Int.* 2011, 209(1-3):86-95.

34) Wright, D.M., Bradley, M.J., Mehltretter, A.H. Analysis and discrimination of single-layer white architectural paint samples, *J. For. Sci.* 2013, 58 (2):358-364.

35) Zawodny C.P., Wampler, T.P. Tools of the trade. *Adhesives Age* June 1999.

36) Zhang, Y., Xia, Z., Huang, H., and Chen, H. Thermal degradation of polyurethane based on IPDI. *J. Anal. Appl. Pyrolysis* 2009; 84:89-94.

Rev. #	Issue Date	History
5	11/15/19	Editorial changes throughout; Section 5 – Added a procedural step and clarity to other steps Section 6 – Edited instrumental conditions Section 7 – Modified Decision Criteria to describe how blanks and samples are evaluated and documented Section 10 – Edited limitations
6	05/03/21	Added solvents to equipment list to align with procedural guidance. Removed the term "reference collections" from Section 3. Section 7.2 – edited to align with OSAC comparative data language. Minor formatting edits throughout.

Approval

Redacted - Signatures on File

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